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THE EFFECT OF DOPING ON THE THERMAL DECOMPOSITION OF SODIUM BROMATE

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ABSTRACT

The thermal decomposition of sodium bromate doped with potassium bromate and sodium bromide, each in the mole fraction range 10^{-4}–10^{-1}, was studied by thermogravimetry. The activation energy, frequency factor and entropy of activation were computed using the Coats–Redfern, Freeman–Carroll and Horowitz–Metzger methods. Doping enhances the decomposition and decreases the energy of activation, the effect increasing with increase in concentration of the dopant. The mechanism of decomposition follows the Avrami equation, $1-(1-\alpha)^{1/3}=kt$, and the rate-controlling process is a phase-boundary reaction assuming spherical symmetry.

INTRODUCTION

A considerable amount of work has been done on the influence of irradiation on the thermal decomposition of alkali and alkaline earth bromates [1–4]. It has been found that irradiation generally increases the rate of thermal decomposition, lowering the energy of activation. The effect of irradiation was attributed to lattice defects and chemical damage fragments, as well as to the chemical products of decomposition. It was of interest therefore to investigate the role of defects as different from that of the product chemical species under irradiation. This can be done by introducing defects in the crystal by doping with cations and anions. Sodium bromate which was used to study the effect of irradiation on the thermal decomposition [2] was chosen for this study with potassium bromate and sodium bromide as the dopants. Dynamic thermogravimetry was used as before because of its advantages over the isothermal method [5].

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EXPERIMENTAL

Material

AnalaR grade sodium bromate, potassium bromate and sodium bromide (Fluka) were used without further purification. Crystals of sodium bromate doped with potassium bromate and sodium bromide, each in the mole fraction range 10^{-4}–10^{-1}, were prepared by slow crystallisation of solutions containing calculated amounts of sodium bromate and potassium bromate, and sodium bromate and sodium bromide, respectively. The products were separated under suction, washed five times with small amounts of cold water and dried in vacuo over P_2O_5. The concentration of bromate was determined by the method of Britton and Britton [6], bromide was determined by micro-argentometric titration after treatment with excess arsenite to reduce the bromate [7], and sodium and potassium were analysed by flame photometry [8]. The structure of the doped crystals was examined, but no changes in the position or intensities of the lines could be detected for the impurity levels used in these investigations. The doped crystals were ground and sieved, and crystals in the 200–240 mesh range were collected and stored in vacuo over P_2O_5 and were used for the decomposition studies.

TG studies

Thermograms of both untreated and doped samples were recorded in nitrogen using a Dupont automatically recording thermal analyser model 990 with TG model 951. Dry nitrogen was purged at a rate of 50 cm^3 min^{-1}. The heating rate was 10 °C min^{-1}. In all experiments, 10 mg samples were used. The recorded total mass loss in all cases was 3.18 ± 0.05 mg, confirming the complete conversion to sodium bromide. The mass of material left behind after decomposition agreed with the instrument reading.

The thermal decomposition of untreated sodium bromate (sample 1), sodium bromate doped with potassium bromate (samples 2–4) and sodium bromate doped with sodium bromide (samples 5–8) was studied.

RESULTS

The recorded TG traces were redrawn as mass vs. temperature (TG) curves and are presented in Figs. 1 and 2. The initial mass of the sample in all cases is normalised to 100 mg. All the TG curves present the same pattern. The decomposition in the doped samples proceeds faster (curves 2–4 in Fig. 1 and curves 2–5 in Fig. 2). Replacement of nitrogen by air had no effect on the decomposition. Three non-isothermal runs were taken for each sample and the mass-loss–temperature relationship was reproducible.

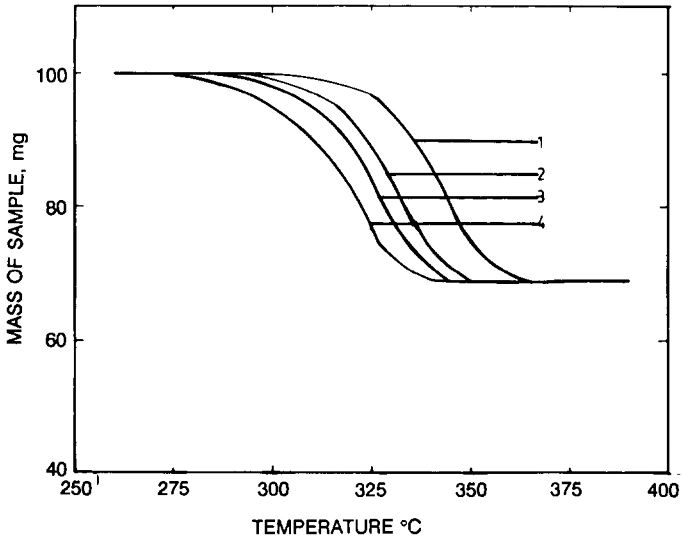

Fig. 1. TG curves of sodium bromate: 1, untreated; 2, doped with 10^{-3} M potassium bromate; 3, doped with 10^{-2} M potassium bromate; 4, doped with 10^{-1} M potassium bromate.

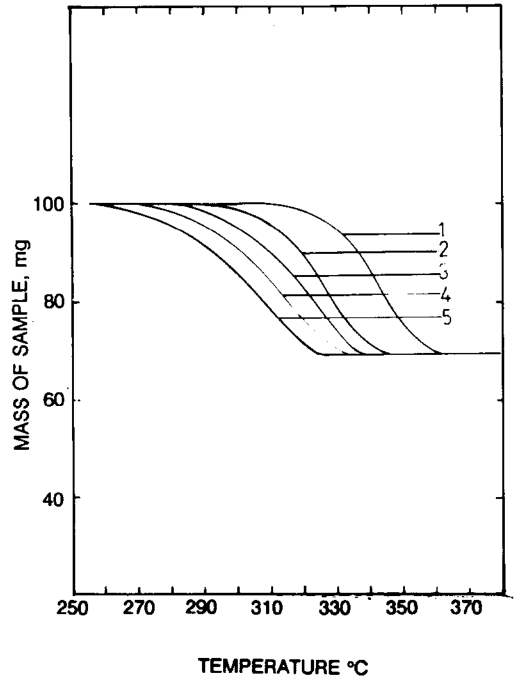

Fig. 2. TG curves of sodium bromate: 1, untreated; 2, doped with 10^{-4} M sodium bromide; 3, doped with 10^{-3} M sodium bromide; 4, doped with 10^{-2} M sodium bromide; 5, doped with 10^{-1} M sodium bromide.

TABLE 1

Kinetic parameters calculated using the Coats–Redfern (CR), Freeman–Carroll (FC) and Horowitz–Metzger (HM) equations

	T_i (K)	T_f (K)	T_s (K)	Kinetic parameters											
				Coats–Redfern (CR)				Freeman–Carroll (FC)				Horowitz–Metzger (HM)			
				E (kJ mol^{-1})	Z (s^{-1})	ΔS (J K^{-1} mol^{-1})	r	E (kJ mol^{-1})	Z (s^{-1})	ΔS (J K^{-1} mol^{-1})	r	E (kJ mol^{-1})	Z (s^{-1})	ΔS (J K^{-1} mol^{-1})	r
1. $NaBrO_3$	583	633	618	344.7	2.7×10^{28}	293.3	0.9981	369.4	6.9×10^{30}	339.4	0.9959	366.5	5.4×10^{30}	337.4	0.9970
2. $NaBrO_3$ doped with $KBrO_3$ (10^{-3} M)	573	623	608	308.3	6.8×10^{25}	243.7	0.9921	316.4	6.6×10^{26}	262.2	0.9786	327.8	7.7×10^{27}	283.1	0.9900
3. $NaBrO_3$ doped with $KBrO_3$ (10^{-2} M)	563	618	598	285.5	1.2×10^{24}	210.3	0.9966	290.7	6.7×10^{24}	224.6	0.9738	302.3	1.3×10^{26}	249.1	0.9948
4. $NaBrO_3$ doped with $KBrO_3$ (10^{-1} M)	553	613	598	255.0	4.2×10^{21}	163.2	0.9971	265.5	7.0×10^{22}	186.7	0.9837	278.3	9.5×10^{23}	208.3	0.9957
5. $NaBrO_3$ doped with NaBr (10^{-4} M)	573	618	608	294.2	6.5×10^{24}	224.2	0.9956	296.5	2.2×10^{25}	234.3	0.9913	299.5	2.6×10^{5}	235.8	0.9991
6. $NaBrO_3$ doped with NaBr (10^{-3} M)	563	608	603	247.6	1.0×10^{21}	151.6	0.9961	238.8	3.6×10^{20}	142.9	0.9912	260.0	1.4×10^{22}	173.4	0.9977
7. $NaBrO_3$ doped with NaBr (10^{-2} M)	553	603	593	216.0	2.7×10^{18}	102.1	0.9964	212.6	2.8×10^{18}	102.5	0.9910	214.2	2.7×10^{18}	102.3	0.9992
8. $NaBrO_3$ doped with NaBr (10^{-1} M)	543	598	593	186.6	9.4×10^{15}	55.2	0.9977	187.5	2.3×10^{16}	62.8	0.9910	198.1	9.6×10^{16}	74.5	0.9990

It was earlier seen [2] that the decomposition of sodium bromate follows first-order kinetics; therefore, the kinetic parameters for the decomposition of sodium bromate and the doped samples in the present study were calculated using the Coats–Redfern [9] and Freeman–Carroll [10] equations, in the form applicable for a first-order process, and also by the Horowitz–Metzger method [11]. The method of computation in each case has been described earlier [12].

The results of the analysis of the data are presented in Table 1. The values of the activation energy E obtained by using the three equations show good agreement, within about 10%.

DISCUSSION

Sodium bromate decomposes according to the equation [13]

$$NaBrO_3 \rightarrow NaBr + 3/2O_2 \tag{1}$$

The decomposition in the present studies begins at 310 °C, in agreement with that observed earlier [2]. Doping lowers the temperature at which the decomposition begins, T_i, by 10, 20 and 30 °C in samples doped with potassium bromate at concentrations of 10^{-3}, 10^{-2} and 10^{-1} M respectively. T_i is also lowered by 10, 20, 30 and 40 °C in samples of sodium bromate doped with sodium bromide at concentrations of 10^{-4}, 10^{-3}, 10^{-2} and 10^{-1} M respectively. Similar lowering can be seen in the temperature of completion of decomposition, T_f, and peak temperature, T_s. Thus doping lowers T_i, T_f and T_s as seen in the case of irradiated samples [2].

It is evident from Table 1 that the activation energy decreases with increase in concentration of the dopant and that the effect is more pronounced in the case of sodium bromate doped with sodium bromide. The value of E for the decomposition of sodium bromate obtained in the present studies is comparable with that reported in the earlier work [2]. Doping also lowers the entropy of activation ΔS. The decrease in ΔS indicates that the decomposition is catalysed in the doped samples as has been reported in the case of irradiated sodium bromate [2].

It has been found that homovalent impurities can produce vacancies [14] or act as electron traps [15], and that such homovalent additions affect the initial retention and sensitivity to thermal annealing of neutron irradiation damage in potassium chromate [16] and mixed crystals of potassium dihydrogen phosphate and arsenate [17]. The higher susceptibility of the potassium-doped sodium bromate to thermal decomposition is therefore due to the presence of lattice defects. The vacancies generate free space and local strain, and the strain distorts the structure of the crystal and alters the frequency of the phonon vibration in the lattice [18,19]. The relaxation time also changes in the region of the lattice surrounding the defect and a

TABLE 2

Kinetic parameters for decomposition of sodium bromate doped with potassium bromate (10^{-3}–10^{-1} M) and sodium bromate doped with sodium bromide (10^{-4}–10^{-1} M) using the mechanism-based equation $1-(1-\alpha)^{1/3}=kt$

Parameter	$NaBrO_3$ (pure)	$NaBrO_3$ doped with $KBrO_3$			$NaBrO_3$ doped with NaBr			
		10^{-3} M	10^{-2} M	10^{-1} M	10^{-4} M	10^{-3} M	10^{-2} M	10^{-1} M
Slope	−39.1	−34.6	−32.5	−29.0	−32.9	−27.8	−24.4	−21.0
Intercept	61.8	55.6	52.6	47.3	53.1	45.5	40.1	34.8
Correlation coefficient	0.9941	0.9855	0.9914	0.9929	0.9889	0.9939	0.9938	0.9966
E (kJ mol^{-1})	335.4	297.8	279.8	250.7	283.0	241.0	212.0	183.9
Z (s^{-1})	6.9×10^{26}	1.4×10^{24}	7.0×10^{22}	3.4×10^{20}	1.2×10^{23}	5.5×10^{19}	2.6×10^{17}	1.3×10^{15}

decrease in the symmetry of the host (bromate) ions occurs. These factors substantially weaken the chemical bonds in the vicinity of the defect thereby increasing the reactivity of the solid decomposition.

However, in the case of sodium bromate doped with sodium bromide, the presence of Br^- facilitates formation of the eutectic between the bromate and bromide [20] with greater ease compared with the untreated sample, thus enhancing the decomposition in the doped samples.

The mechanism of the thermal decomposition reaction of the untreated and doped samples of sodium bromate was established by following the non-isothermal method discussed by Sestak and Berggren [21] and Satava [22]. The details regarding the computational approach for obtaining the correct mechanism and the corresponding E and Z values have already been discussed [12]. The functional values of $\ln g(\alpha)$ required for this purpose were taken from the table of Nair and James [23] and E was calculated by the method of Sestak [24]. For almost the same value of correlation coefficient, r, the operating mechanism was chosen by non-mechanistic equation. It was found that the R_3 mechanism [21] gives the maximum correlation (Table 2).

It is evident from Table 2 that the decomposition of sodium bromate (both untreated and doped samples) follows the Avrami equation [25], $1-(1-\alpha)^{1/3}=kt$ and that the rate-controlling process is a phase-boundary reaction assuming spherical symmetry [22].

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